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Antimonides with $D8_8$ and Hf_5Sn_3Cu Structure Types

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The crystal structures of eight binary rare earth antimonides of composition R_5Sb_3 are found to be of the $D8_8$ structure type. Seven ternary compounds of composition R'_5Sb_3X (where R′ = Ti, Zr, Hf and X = Ni, Cu, Zn) select the Hf_5Sn_3Cu structure type, a filled up version of the $D8_8$ structure type.

In continuation of an intensive research program (Jeitschko & Parthé, 1967; Jeitschko & Parthé, 1965; Schob & Parthé, 1964), to investigate the occurrence and stability of the $D8_8$ structure type, we studied the crystal structures of binary rare earth antimonides of composition R_5Sb_3 and Ni, Cu-, Zn-stabilized antimonides of Ti, Zr and Hf of composition $(Ti,Zr,Hf)_5Sb_3(Ni,Cu,Zn)$.

The rare earth antimonides were prepared by melting the components under argon atmosphere and at low excitation voltages in an arc melting furnace. The compositions were controlled by checking the weight losses during the preparation; they were found to be negligible. The ternary Ti, Zr and Hf compounds were prepared by sintering stoichiometric mixtures in evacuated silica tubes for up to eight weeks at 800°C.

Rare earth antimonides

All rare earth compounds could be indexed with hexagonal unit cells and lattice constants as given in Table 1. These compounds crystallize with the normal $D8_8$ structure type: space group $P6_3/mcm$ (D^3_{6h}) with four R atoms in 4(d), six R atoms in 6($g_{\rm I}$) with $x_{\rm I} \sim 0{\cdot}25$, and 6Sb in 6($g_{\rm II}$) with $x_{\rm II} \sim 0{\cdot}61$. The structure of Ho_5Sb_3 has been refined from powder diffractometer tracings, using 46 observed and unobserved reflections and the least-squares program by Gantzel, Sparks & Trueblood (1961). The final parameters are $x_{\rm Ho} = 0{\cdot}2437 \pm 0{\cdot}0002$, $x_{\rm Sb} = 0{\cdot}6085 \pm 0{\cdot}0003$. The isotropic temperature factor B of Ho was found to be 1·2, and the isotropic temperature factor B of Sb was calculated to be 0·4.

The R value $\Sigma\,||F_{\rm obs}| - |F_{\rm calc}||/\Sigma\,|F_{\rm obs}|$ was found to be 0·097. The intensity calculation for Ho_5Sb_3 using the new parameters is given in Table 2.

Table 2. *Intensity calculation for* Ho_5Sb_3 *with* $D8_8$ *structure type*

Cu $K\alpha_1$ radiation $x_{\rm Ho} = 0{\cdot}2437$, $B_{\rm Ho} = 1{\cdot}20$
($\lambda = 1{\cdot}54051$ Å) $x_{\rm Sb} = 0{\cdot}6085$, $B_{\rm Sb} = 0{\cdot}40$.

hkil	d_c	$10^3 \sin^2\theta_c$	$10^3 \sin^2\theta_o$	I_c	I_o
$10\bar{1}0$	7·665	10·10	10·04	45·8	45
$11\bar{2}0$	4·425	30·29	30·15	0·5	< 8
$20\bar{2}0$	3·832	40·39	40·43	64·5	22
$11\bar{2}1$	3·608	45·56	45·74	5·8	< 8
0002	3·116	61·07	61·01	161·3	281
$21\bar{3}0$	2·897	70·68	70·70	339·7	471*
$10\bar{1}2$	2·887	71·17	71·42	197·0	
$21\bar{3}1$	2·627	85·95	85·97	1000·0	1000
$30\bar{3}0$	2·555	90·87	90·63	451·7	1323*
$11\bar{2}2$	2·548	91·36	91·63	782·7	
$20\bar{2}2$	2·418	101·46	101·42	51·0	84
$22\bar{4}0$	2·212	121·16	—	6·0	< 8
$31\bar{4}0$	2·126	131·26	131·36	31·3	40
$21\bar{3}2$	2·122	131·75		1·4	
$22\bar{4}1$	2·085	136·43	136·72	61·9	71
$31\bar{4}1$	2·012	146·53	146·44	84·2	113
$30\bar{3}2$	1·976	151·94	152·05	0·8	< 8
$40\bar{4}0$	1·916	161·55	161·86	18·2	13
$11\bar{2}3$	1·880	167·70	—	0·5	< 8
$22\bar{4}2$	1·804	182·23	186·4	188·9	174
$32\bar{4}0$	1·758	191·84	192·14	6·1	29
$31\bar{4}2$	1·756	192·33		26·0	
$32\bar{5}1$	1·692	207·11	207·23	107·4	340*
$21\bar{3}3$	1·688	208·09	208·51	239·7	

Table 1. R_5Sb_3 *phases with* $D8_8$ *structure type*

	a	*c*	*c/a*	*V*	Reference*
La_5Sb_3	9·42 ± 0·01	6·62 ± 0·01	0·703	508·7	(1)
Ce_5Sb_3	9·302 ± 0·009	6·514 ± 0·005	0·7003	488·1	(1)
Pr_5Sb_3	9·233 ± 0·004	6·510 ± 0·004	0·7050	480·6	(1)
Nd_5Sb_3	9·180 ± 0·005	6·463 ± 0·005	0·7041	471·7	(1)
Gd_5Sb_3	8·975 ± 0·004	6·343 ± 0·003	0·7067	442·5	(1)
Tb_5Sb_3	8·920 ± 0·003	6·304 ± 0·003	0·7067	434·4	(1)
Dy_5Sb_3	8·870 ± 0·004	6·266 ± 0·003	0·7064	427·0	(1)
Ho_5Sb_3	8·851 ± 0·002	6·234 ± 0·002	0·7043	423·0	(1)
Yb_5Sb_3	8·995	6·870	0·764	481·4	(2)

* (1) This work. (2) Bodnar & Steinfink, 1967.

Table 2 (*cont.*)

hkil	d_c	$10^3 \sin^2 \theta_c$	$10^3 \sin_o \theta^2$	I_c	$_oI$
$41\bar{5}0$	1·672	212·03	212·49	86·8	60
$40\bar{4}2$	1·632	222·62	222·87	123·4	83
$41\bar{5}1$	1·615	227·30	—	6·1	< 8
0004	1·558	244·29	244·43	87·3	130
$50\bar{5}0$	1·533	252·42	252·58	33·7	97*
$32\bar{5}2$	1·531	252·91	253·02	34·4	
$10\bar{1}4$	1·527	254·38	—	0·9	< 8
$22\bar{4}3$	1·514	258·57	259·07	21·0	22
$31\bar{4}3$	1·486	268·67	268·67	30·5	45
$33\bar{6}0$	1·475	272·61	273·78	4·0	30
$41\bar{5}2$	1·473	273·10		28·7	
$11\bar{2}4$	1·470	274·58	—	0·0	< 8*
$42\bar{6}0$	1·448	282·71	282·69	66·3	65
$20\bar{2}4$	1·443	284·67	284·27	5·2	
$33\bar{6}1$	1·435	287·88	287·90	63·1	53
$42\bar{6}1$	1·411	297·98	298·23	28·1	32
$51\bar{6}0$	1·376	313·00	313·51	25·2	190
$50\bar{5}2$	1·375	313·49		135·4	
$21\bar{3}4$	1·372	314·96	315·13	55·3	72
$51\bar{6}1$	1·344	328·27	328·66	48·3	96
$32\bar{5}3$	1·342	329·25		44·8	
$33\bar{6}2$	1·333	333·68	334·25	45·3	150*
$30\bar{3}4$	1·330	335·16	335·57	97·7	
$42\bar{6}2$	1·313	343·78	343·83	10·8	13
$41\bar{5}3$	1·303	349·44	—	2·8	< 8
$60\bar{6}0$	1·277	363·48	—	1·9	< 8
$22\bar{4}4$	1·274	365·45	—	1·5	< 8
$43\bar{7}0$	1·260	373·58	—	2·9	< 8
$51\bar{6}2$	1·259	374·07	—	0·0	< 8
$31\bar{4}4$	1·256	375·54	—	10·4	21
$43\bar{7}1$	1·235	388·85	389·23	15·8	17
$52\bar{7}0$	1·227	393·78	393·48	13·1	8
$40\bar{4}4$	1·209	405·83	—	5·9	< 8
$52\bar{7}1$	1·204	409·04	410·09	35·2	60
$33\bar{6}3$	1·202	410·02		32·4	

* For these line pairs it was possible to measure the individual θ values but only a common intensity value.

In Fig. 1 are plotted the cube roots of the volume of one formula unit R_5Sb_3 *versus* the 3-valent ionic radii of the rare earth elements in a way which we have discussed before (Hohnke & Parthé, 1966; Parthé, 1967). The slope of the data points indicates that the electronic state of the rare earth metals in these compounds is the same except for Yb which shows an extraordinarily big deviation. The deviation is also found with the axial ratio as can be seen in Table 1, where the c/a index for Yb_5Sb_3 is 0·764, whereas the c/a ratio for the other compounds is $\sim$0·707.

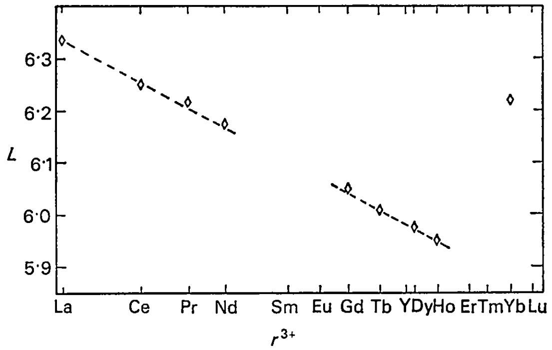

Fig. 1. Cube roots of the formula units of R_5Sb_3 compounds with $D8_8$ structure type *versus* the 3-valent ionic radii of the rare earth metals.

Ni, Cu- or Zn-stabilized antimonides of Ti, Zr and Hf

All these compounds could again be indexed with hexagonal unit cells, and lattice constants as given in Table 3. The extinctions are the same as for the $D8_8$ structure type ($h0\bar{h}l$ with $l=2n+1$); however, the structure is now a filled up version of the $D8_8$ structure type as described for Hf_5Sn_3Cu. (Rieger, Nowotny & Benesovsky, 1965): space group $P6_3/mcm$ (D_{6h}^3) with 4 Hf in 4(*d*), 6 Hf in 6(g_I) with $x_I \sim 0{\cdot}27$, 6 Sb in 6(g_{II}) with $x_{II} \sim 0{\cdot}61$, 2 Cu in 2(*b*). An intensity calculation using these parameters was made for Hf_5Sb_3Zn as shown in Table 4. The agreement is excellent; it was not felt necessary to perform a refinement on this structure.

Table 3. *Ternary antimonides with* Hf_5Sn_3Cu *type, a filled-up version of the* $D8_8$ *structure type*

	a	*c*	*c/a*	*V*
Ti_5Sb_3Cu	8·020 ± 0·010	5·515 ± 0·010	0·687	307·2
Zr_5Sb_3Ni	8·530 ± 0·005	5·773 ± 0·005	0·677	363·8
Zr_5Sb_3Cu	8·526 ± 0·007	5·786 ± 0·005	0·679	364·3
Zr_5Sb_3Zn	8·555 ± 0·007	5·820 ± 0·005	0·680	368·9
Hf_5Sb_3Ni	8·469 ± 0·004	5·715 ± 0·004	0·675	355·0
Hf_5Sb_3Cu	8·476 ± 0·004	5·724 ± 0·004	0·675	356·1
Hf_5Sb_3Zn	8·514 ± 0·003	5·747 ± 0·003	0·675	360·8

Table 4. *Intensity calculation for* Hf_5Sb_3Zn *with* Hf_5Sn_3Cu *structure type*

Cr $K\alpha$ radiation. $x_{Hf}=0{\cdot}270$, $x_{Sb}=0{\cdot}610$.

hkil	d_c	$10^3 \sin^2 \theta_c$	$10^3 \sin^2 \theta_o$	I_c	I_o
$10\bar{1}0$	7·3733	24·13	—	21	—
$11\bar{1}0$	4·2570	72·40	—	6	—
$20\bar{2}0$	3·6867	96·54	—	28	—
$11\bar{2}1$	3·4208	112·13	113·6	60	*vvw*
0002	2·8735	158·90	160·3	102	*vw*
$21\bar{3}0$	2·7869	168·94	170·7	153	*w*
$10\bar{1}2$	2·6774	183·04	184·0	67	*vw*
$21\bar{3}1$	2·5076	208·67	210·4	719	*s*
$30\bar{3}0$	2·4578	217·21	219·0	801	*s+*
$11\bar{2}2$	2·3817	231·31	232·8	1000	*vs*
$20\bar{2}2$	2·2664	255·44	—	16	—
$22\bar{4}0$	2·1285	289·61	—	15	—
$31\bar{4}0$	2·0450	313·74	—	3	—
$21\bar{3}2$	2·0005	327·84	—	1	—
$22\bar{4}1$	1·9960	329·34	—	< 1	—
$31\bar{4}1$	1·9267	353·47	355·5	149	*m*
$30\bar{3}2$	1·8678	376·11	—	11	—
$40\bar{4}0$	1·8433	386·15	—	26	—
$11\bar{2}3$	1·7469	429·94	—	9	—
$22\bar{4}2$	1·7104	448·51	449·5	272	*s−*
$32\bar{5}0$	1·6916	458·55	—	9	—
$31\bar{4}2$	1·6661	472·65	473·0	30	*vw*
$32\bar{5}1$	1·6227	498·27	499·1	152	*m+*
$41\bar{5}0$	1·6090	506·82	507·7	68	*wm*
$21\bar{3}3$	1·5787	526·47	527·5	201	*ms*
$40\bar{4}2$	1·5515	545·05	546·2	123	*m*
$41\bar{5}1$	1·5494	546·54	—	2	—
$50\bar{5}0$	1·4747	603·35	—	10	—
$32\bar{5}2$	1·4577	617·45	—	8	—
0004	1·4367	635·62	636·1	137	*m+*
$22\bar{4}3$	1·4239	647·15	—	< 1	—
$33\bar{6}0$	1·4190	651·62	—	53	*w*

Table 4 (*cont.*)

hkil	e_c	$10^3 \sin^2 \theta_c$	$10^3 \sin^2 \theta_o$	I_c	I_o
$10\bar{1}4$	1·4102	659·75	—	1	—
$41\bar{5}2$	1·4039	665·72	666·1	223	*s*−
$31\bar{4}3$	1·3981	671·28	671·0	87	*m*
$42\bar{6}0$	1·3934	675·76	675·9	82	*m*
$33\bar{6}1$	1·3776	691·35	691·4	49	*w*
$11\bar{2}4$	1·3613	708·02	—	< 1	—
$42\bar{6}1$	1·3542	715·48	716·0	183	*ms*
$20\bar{2}4$	1·3387	732·16	732·2	6	*vw*
$51\bar{6}0$	1·3243	748·16	748·5	89	*m*
$50\bar{5}2$	1·3120	762·26	762·7	99	*m*
$51\bar{6}1$	1·2905	787·88	788·0	289	*s*
$21\bar{3}4$	1·2770	804·56	805·0	77	*wm*
$33\bar{6}2$	1·2723	810·53	811·0	81	*wm*
$32\bar{5}3$	1·2680	816·08	816·0	174	*ms*
$42\bar{6}2$	1·2538	834·66	834·6	44	*vw*
$30\bar{3}4$	1·2404	852·83	852·3	633	*vs*
$41\bar{5}3$	1·2321	864·35	—	3	—
$60\bar{6}0$	1·2289	868·83	868·6	39	*vw*
$43\bar{7}0$	1·2122	892·96	—	25	—
$51\bar{6}2$	1·2027	907·06	906·5	59	*vw*
$22\bar{4}4$	1·1908	925·23	925·5	26	*vvw*
$43\bar{7}1$	1·1861	932·69	932·9	43	*vw*
$52\bar{7}0$	1·1807	941·23	940·8	177	*m*

The similarity of the X-ray patterns indicates that all the other compounds listed in Table 3 were of the same structure type.

Discussion

Stable binary antimonides with $D8_8$ structure seem to form only with the rare earth elements. The earlier reported Zr_5Sb_3 (Boller & Parthé, 1963) is extremely unstable; it decomposes in air within half an hour. It seems that Ti_5Sb_3 and Hf_5Sb_3 do not form at all. However, all these fourth-group antimonides can be stabilized by addition of Ni, Cu or even Zn atoms which then occupy octahedral voids in the structure. Our experiments indicate that these three elements are the only ones to stabilize the $D8_8$ structure with the fourth-group antimonides. In particular, it was found impossible to use C, B, Fe, Co, Mn, Ru, Pt or Ir as stabilizers. In this connection, it should be mentioned that V_5As_3 does not exist as binary $D8_8$ phase but must be stabilized by carbon (Boller & Nowotny, 1966). Whether a particular stabilizing atom can be used or not depends, it seems, upon the size of the octahedral void.

A detailed discussion about the occurrence of all representatives of the $D8_8$ and related structure types will be given at a later time.

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References

BODNAR, R. E. & STEINFINK, H. (1967). *Inorg. Chem.* **6**, 327.

BOLLER, H. & NOWOTNY, H. (1966). *Mh. Chem.* **97**, 1053.

BOLLER, H. & PARTHÉ, E. (1963). *Mh. Chem.* **94**, 225.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Program UCLA-LS 1.

HOHNKE, D. & PARTHÉ, E. (1966). *Acta Cryst.* **21**, 435.

JEITSCHKO, W. & PARTHÉ, E. (1965). *Acta Cryst.* **19**, 275.

JEITSCHKO, W. & PARTHÉ, E. (1967). *Acta Cryst.* **22**, 551.

PARTHÉ, E. (1967). In *Propriétés Thermodynamiques, Physiques et Structurales des Dérivés Semi-Metalliques.* Colloques Internationaux du Centre National de la Recherche Scientifique, No. 157, pages 195–205. Paris: Editions du CNRS.

RIEGER, W., NOWOTNY, H. & BENESOVSKY, F. (1965). *Mh. Chem.* **96**, 98, 232.

SCHOB, O. & PARTHÉ, E. (1964). *Acta Cryst.* **17**, 1335.